



Atomic and electronic structures of graphene-decorated graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) as a metal-free photocatalyst under visible-light

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ABSTRACT

Industrial demands for sustainable and renewable energy resources have inspired studies on photonic and electronic properties of graphitic-carbon nitride ($g\text{-C}_3\text{N}_4$) as a promising photocatalyst without precious metal. The absorption and the yield by metal-free pristine $g\text{-C}_3\text{N}_4$ are, however, still limited with hydrogen/oxygen evolution reaction (HER/OER) mostly around ultraviolet-light. Here, we propose the graphene-decorated $g\text{-C}_3\text{N}_4$ as a metal-free photocatalyst under visible-light, based on our atomic-scale measurements and calculations. The $g\text{-C}_3\text{N}_4$ nanosheets on highly-oriented pyrolytic graphite (HOPG) exhibit band-gaps appropriate for visible-light absorption and work-functions tuned for band alignments to supply electrons and holes for HER/OER. Scanning probe microscopy (SPM) measurements for local density of states (LDOS) in atomic scale and work-functions in nanometer scale with *ab initio* calculations confirmed the various electronic transitions for each nitrogen and carbon atom in different atomic registries. The graphene-decorated $g\text{-C}_3\text{N}_4$, therefore, could provide a breakthrough enabling the efficient water-splitting reactions under visible-light without precious metal.

1. Introduction

Hydrogen evolution reaction (HER) by water-splitting has been intensively studied for fuel cells as clean and renewable energy resources [1–11]. However, the applications are hindered by the significantly high cost owing to the inevitable usage of precious metals as catalytic and antioxidant electrodes in electrolysis or photocatalysis, which has inspired extensive studies to reduce the amount of precious metals by mixing catalytic materials such as polymeric carbon nitride (PCN) [12–17]. Among many allotropes of carbon nitrides, graphitic-carbon nitride ($g\text{-C}_3\text{N}_4$) is known to be the most stable phase under ambient conditions [18,19]. $g\text{-C}_3\text{N}_4$ is a graphitic phase of PCN polymerized from triazine or heptazine as a unit molecule. It has been reported that water

can be dissociated by pristine $g\text{-C}_3\text{N}_4$ nanosheets under ultraviolet light [20]. Although it is challenging, it is required to improve the electronic properties of $g\text{-C}_3\text{N}_4$ to increase the efficiency of photocatalytic reactions under visible light without precious metals. In this study, we propose a new model system of graphene-decorated $g\text{-C}_3\text{N}_4$, which can be applied for the metal-free hydrogen evolution under visible light. We revealed that the graphene-decorated $g\text{-C}_3\text{N}_4$ has a direct band-gap of 2.51 eV and indirect band-gap of 1.64 eV. The band-gap-engineered electric properties of this metal-free catalyst were confirmed by scanning tunneling microscopy and spectroscopy (STM/STS) and Kelvin probe force microscopy (KPFM) along with density functional theory (DFT) calculations, which explain the electronic structures of the system as a photocatalyst under visible light at the atomic scale.

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2. Experimental

2.1. Preparation of g-C₃N₄ nanosheets

The cyanamide, CH₂N₂ (0.3 g, Alfa Aesar Chemical Co. Ltd. Korea) as a precursor for g-C₃N₄ was immobilized in the interlayer space of expandable synthetic clay with chemical formula Na_{0.7}Mg_{2.65}Si₄O₁₀F₂ (1 g, CO-OP Chemical Co. Ltd. Japan) under a reaction condition of 100 °C for 3 h, and then thus prepared cyanamid-clay hybrid derivative was further heated up to 550 °C to realize the formation of g-C₃N₄ in the 2D clay lattice. Finally, the nanosheet g-C₃N₄ was separated out from g-C₃N₄-clay hybrid simply by dissolving clay only in hydrofluoric acid at 0 °C for 4 h. The fluorinated impurity possibly on nanosheet g-C₃N₄ was also removed by hydrochloric acid at 80 °C for 1 h. Thus, obtained suspension was washed with deionized water to remove the residual acid. The bulk g-C₃N₄, as a control, was also prepared by heating the cyanamide at 550 °C for 4 h with the heating rate of 3 °C/min [21].

2.2. Characterization of g-C₃N₄ nanosheets

The X-ray diffraction (XRD) patterns for the samples were recorded with a Rigaku RINT-Ultima III diffractometer using Ni-filtered Cu-K α radiation (λ = 1.5405 Å) operated at 40 kV and 30 mA. The diffuse reflectance UV-vis spectra were measured with Jasco V-550 spectrophotometer equipped with an integrating sphere by using BaSO₄ plate as a baseline. Fourier transform infrared (FT-IR) spectra were obtained from Jasco FT/IR 6100 spectrophotometer by using KBr pellet method. Electron energy loss spectroscopy (EELS) analyses were performed using a JEM ARM-200 F microscope equipped with an EELS detector (965 GIF Quantum ER, GATAN, US) at 80 kV. According to XRD analyses for the bulk g-C₃N₄ and g-C₃N₄ nanosheets as shown in Figure S1(a), the peak at 27.5° corresponding to the (002) plan was observed in both cases, though the peak intensity for the latter was significantly reduced due to the fact that the g-C₃N₄ nanosheets were restacked with a limited degree with the thickness of \sim 4.2 nm. To explore the difference in molecular structure of the g-C₃N₄ nanosheets compared to the bulk g-C₃N₄, FT-IR spectroscopic studies were performed as shown in Figure S1(b) and Table S1. The overall spectral feature for both samples were turned out to be the same except a peak at 2170 cm⁻¹, which can be attributed to cyano terminal groups such as C \equiv N and N = C=N, probably due to the formation of small fragment of diazo groups on the surface of g-C₃N₄ nanosheets [22,23]. The absorption edge of g-C₃N₄ nanosheets in UV-vis DRS (Figure S3(c)) exhibited a remarkable blue shift from 455 to 430 nm compared to the bulk g-C₃N₄, surely due to the quantum size effect. As shown in EELS analysis (Figure S3(d)), the bonding nature of g-C₃N₄ nanosheets was determined to be the sp² type, as can be seen from the strong π^* peaks at C K-edge and N-K-edge, respectively [24]. The atomic ratios of N/C from the EELS analysis for the g-C₃N₄ nanosheets and the bulk g-C₃N₄ were calculated to be 1.31 and 1.32, respectively, which were in good agreement with the theoretical one of 1.33.

Preparation of g-C₃N₄ on HOPG: The g-C₃N₄ nanosheets were dispersed in ethanol, and this colloidal was sprayed on highly oriented pyrolytic graphite (HOPG) by mist-spraying followed by a spin-coater (1 min, 1000 rpm). This sample was annealed at \sim 500 °C for 24 h in the UHV chamber before loaded into the STM head.

2.3. Measurements of STM and STS

Preparation chamber was used to clean ex-situ sample, the base pressure less than 5×10^{-10} torr. Besocke type home-built STM was used to measure STM and STS, the base pressure less than 1×10^{-10} torr. It operated at room temperature and 50 mV at 931 Hz lock-in modulation signal was used for tunneling spectroscopy. A chemically-etched W tip was annealed with an e-beam before use.

2.4. DFT calculations

We performed first-principles calculations based on DFT as implemented in the Vienna ab initio Simulation Package (VASP) [25–28]. We used the Perdew–Burke–Ernzerhof exchange-correlation functional with the projector augmented wave pseudopotentials provided by VASP [29]. All DFT calculations in this work include the van der Waals correction base on the semiempirical form of DFT-D2, suggested by Grimme et al. [30]. The cut-off energy for the plane-wave basis was set as 500 eV and the convergence criterion of atomic force for geometric optimization was set at 0.01 eV/Å. The vacuum region was set as 20 Å to eliminate interactions between periodic boundaries. A Monkhorst pack [31] $4 \times 4 \times 1$ k-point mesh was used for the optimization of the structures and the $32 \times 32 \times 1$ k-point mesh was used for the calculation of DOS.

2.5. Measurements of KPFM

We operated a commercial atomic force microscope (AFM), i.e. a NX10 Model (Park Systems Co.) for topographic and surface potential measurements. A non-contact electric force microscopy (EFM) mode in NX10 was used for Kelvin probe force microscopy (KPFM) measurements with NSC36/Cr-Au tips (MikroMasch Co.) and conductive sample holders for an electrical ground to the samples.

3. Results and discussion

The g-C₃N₄/graphene heterostructure is composed of chemically inert and mechanically robust materials; an efficient HER with g-C₃N₄/graphene was already reported [32,33]. The model system of g-C₃N₄/graphene in this study was prepared by depositing g-C₃N₄ nanosheets on a highly oriented pyrolytic graphite (HOPG) substrate, as described in Methods, Figure S1 and table S1. Although HOPG is a bulk phase, the top layer is floating a bit more with broken symmetry in the c-axis. We measured linear dispersion relation between energy and density of states at the low bias regime in Figure S2. Fig. 1(a) shows an atomic force microscopy (AFM) image; the inset shows the corresponding fast-Fourier-transform (FFT) data. The results imply that all of the g-C₃N₄ nanosheets with different thicknesses are epitaxially deposited on HOPG. Fig. 1(b) shows a high-resolution STM image which was measured on thick g-C₃N₄ flakes. The inset is a DFT-simulated image with the ball-stick model of g-C₃N₄, which shows a good agreement with the measurements. Fig. 1(c) is the STS data showing the change of the electronic structure in the graphene decorated g-C₃N₄ system, and Fig. 1(d) is a three-dimensional plot of the charge distribution for visualizing the overlapped orbital between graphene and g-C₃N₄. The energy range is -0.4 eV to -0.2 eV under 5.0×10^{-6} (electrons / Å³).

Among the large number of reported PCNs, mostly aimed for photoelectronic applications, g-C₃N₄ is considered the most promising material for photocatalysts. A previous study predicted that the heptazine-based g-C₃N₄ has two different stable configurations, as shown in Fig. 2(a) and (b) [34]. One of them is a buckled configuration, shown in Fig. 2(a), while the other is a planar configuration, shown in Fig. 2(b). A negligible difference in crystallography is observed between the buckled and planar phases (only a small mismatch of the lattice constant by 0.2 Å due to buckling), while their electronic structures are distinguishable from each other. The buckled phase has only a direct band-gap of 2.87 eV, while the planar phase has both direct and indirect band-gaps of 2.66 eV and 2.27 eV, respectively. We used only the planar phase of g-C₃N₄ nanosheets in this study, as confirmed by photoluminescence (PL) and STS measurements. The PL spectrum in Fig. 2(c) shows the optical band-gap at 581 nm (2.13 eV), which is very close to the prediction for the indirect band-gap of the planar phase. Moreover, the local density of states (LDOS) measured by STS in Fig. 2(d) shows two distinct band-gaps of 2.20 eV and 2.79 eV, which can be assigned to the indirect and direct band-gaps of the planar phase, respectively.

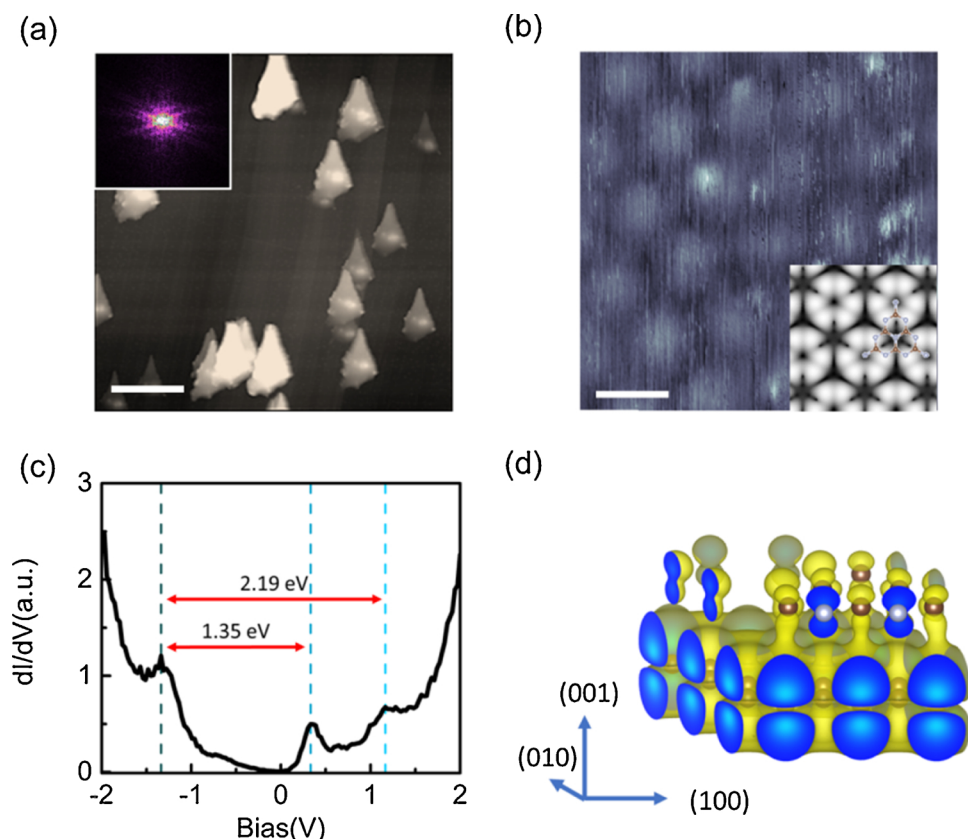


Fig. 1. $g\text{-C}_3\text{N}_4$ /graphene heterostructure for HER. (a) AFM image of $g\text{-C}_3\text{N}_4$ on HOPG; the inset shows the corresponding FFT data. (b) Atomic-resolution STM image of $g\text{-C}_3\text{N}_4$ nanosheets on HOPG with a tunneling current of 0.5 nA and sample bias voltage of -2.0 V. The inset is a DFT-simulated STM image with a ball-stick model of $g\text{-C}_3\text{N}_4$. The scale bars in (a) and (b) correspond to 1 μm and 6.2 nm, respectively. (c) is an average STS of $g\text{-C}_3\text{N}_4$ on HOPG; the indirect and direct band-gaps are indicated. (d) is a three-dimensional plot of electron clouds for the energy range of -0.4 eV to -0.2 eV under 5.0×10^{-6} (electrons / \AA^3).

These spectroscopic data confirm that the $g\text{-C}_3\text{N}_4$ nanosheets in this study mostly exhibit the planar phase.

Careful STS measurements were performed on the different atomic registries of carbon and nitrogen, *i.e.*, carbon (C), nitrogen at the edge

(N_E), nitrogen at the center (N_C), and nitrogen at the bridge (N_B), to investigate the electronic structures of $g\text{-C}_3\text{N}_4$ /graphene heterostructures and understand the origin of HER. The band edges need to be considered to discuss about the absorption band for the external light

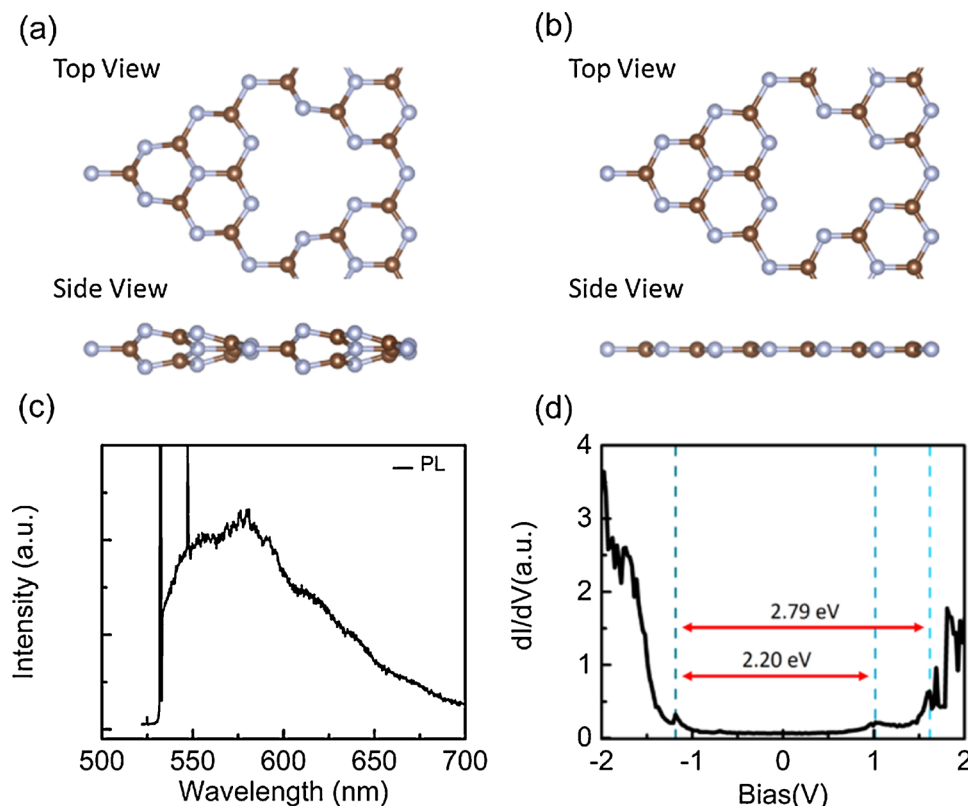


Fig. 2. Phases and electronic structures of the pristine $g\text{-C}_3\text{N}_4$ used in this study. Ball-stick models of the (a) buckled and (b) planar phases of $g\text{-C}_3\text{N}_4$ with top and side views. Carbon and nitrogen atoms are shown in brown and light blue, respectively. (c) PL data of $g\text{-C}_3\text{N}_4$ nanosheets on SiO₂ with sharp peaks from the substrate. (d) STS data measured on a thick $g\text{-C}_3\text{N}_4$ flake with a thickness of 4.2 nm; the indirect and direct band-gaps are indicated. This spectrum was measured with a set-point current of 0.5 nA and lock-in modulation of 50 mV at 931 Hz, at room temperature (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

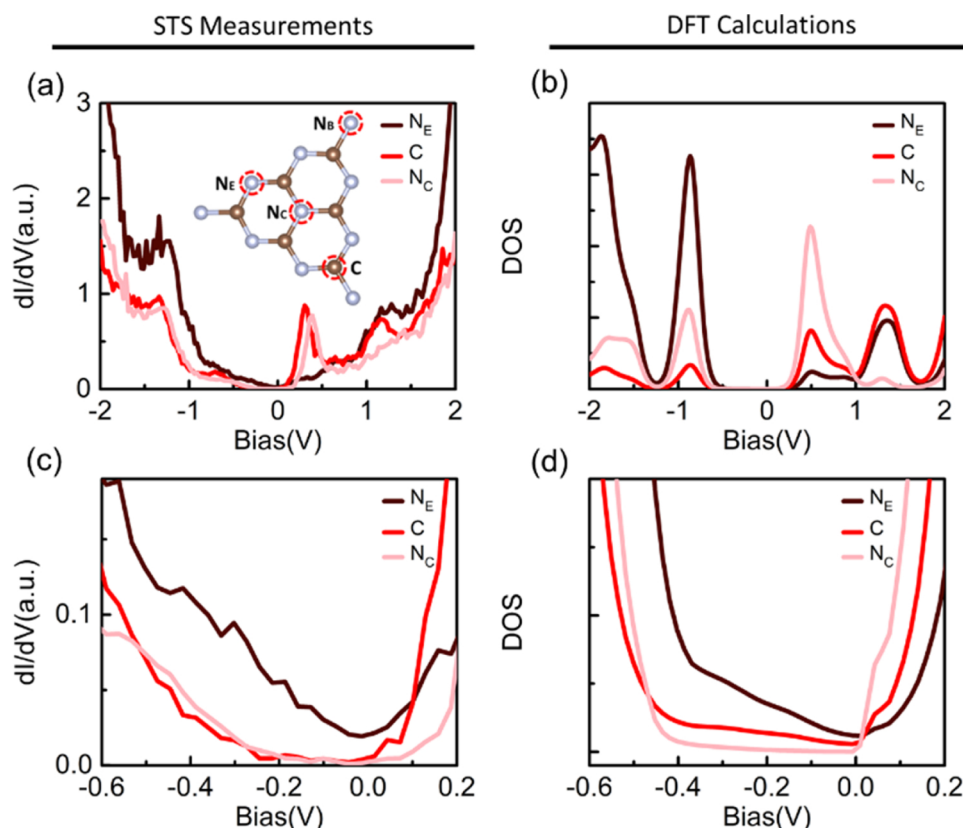


Fig. 3. Figure Caption Measured and calculated electronic structures of g-C₃N₄ at the atomic scale. (a) STS measured on different atomic registries of g-C₃N₄ on HOPG. The inset identifies carbon (C), nitrogen at the edge (N_E), nitrogen at the center (N_C), and nitrogen at the bridge (N_B). (b) DFT calculations for the atomic registries of g-C₃N₄ on HOPG, which show good agreement with Fig. 3(a). (c) and (d) Magnified views of the measured and calculated spectra in Fig. 3(a) and (b) near the Fermi level, respectively. These STS results were measured with a set-point current of 0.5 nA and lock-in modulation of 50 mV at 931 Hz, at room temperature.

[35–41], but the peak position has been analyzed in this work by STS measurements in an atomic scale with DFT calculations to explain shrinking the band-gap with an appropriate workfunction of graphene-decorated g-C₃N₄ for HER applications in a visible light regime.

The inset in Fig. 3(a) illustrates the different atomic registries. Fig. 3(a) shows STS spectra measured on C, N_E , and N_C , while Fig. 3(b) shows the corresponding DFT calculations for each atomic registry, which are in good agreement with each other. The calculations were performed in three different atomic configurations Figure S4 (a)–(c) included the lowest-energy atomic configuration [42]. For conveniences, we named “nitrogen-AB stacking” for (a), “carbon-AB stacking” for (b) and “AA stacking” for (c). However, we didn’t compare all cases due to differences of DOS near the Fermi level. We focused on nitrogen-AB stacking system, the reason will discuss in next paragraph. Compared with the LDOS of the bulk phase in Fig. 2(d), the graphene-decorated g-C₃N₄ exhibits different electronic structures with a narrower band-gap than that of the bulk g-C₃N₄. As illustrated in the inset of Fig. 3(a), all of the carbon atoms have the same local environment, leading to a symmetric bonding with the three nearest-neighbor nitrogen atoms. Similarly, N_C and N_B sites are equivalent, considering only the chemical bonding with the nearest-neighbor carbon atoms of g-C₃N₄. Indeed, we confirmed that these two nitrogen atoms have the same DOS by both experimental measurements and DFT calculations. Therefore, in Fig. 3(a) and (b), we present only the spectrum for N_C . Unlike N_C or N_B , N_E has two additional unpaired electrons, leading to a different LDOS from those of N_C and N_B . The STS in Fig. 3(a) shows three characteristic peaks at approximately -1.34, +0.30, and +1.17 eV, which correspond to -0.86, +0.49, and 1.33 eV in the calculated LDOS in Fig. 3(b), respectively. Compared with the band structure in Figure S5, the peaks around -0.86 eV in Fig. 3(b) can be assigned to the valence band edge at the point. A Dirac point of graphene exists at the point owing to the 33 supercell for hybrid structure calculations. [43] The band-gap between the peaks at -0.86 eV and +0.49 eV corresponds to the indirect band-gap from the (0 0 0) point to

the Y(-0.5 0 0.5) and T(-0.5 0.5 0.5) points. On the other hand, the band-gap between -0.86 eV and +1.33 eV corresponds to the direct band-gap at the point. From these observations, we expect that the excited electrons at N_E should undergo a direct band transition, considering the negligible states at the S point, while the electrons at N_C (as well as N_B) should significantly contribute to an indirect band transition from -0.86 eV to +0.49 eV. Moreover, the excited electrons at N_E can undergo an indirect band transition to the S point of the neighboring carbon atoms of g-C₃N₄. The large number of electrons near N_E can be excited through a direct band-gap of 2.19 eV or indirect band-gap of 1.35 eV by hopping to the nearest-neighbor carbon atoms of g-C₃N₄. This explains the mechanism at the atomic scale that the band-gap of the g-C₃N₄ nanosheets on the HOPG is tuned to the value corresponding to the visible-light regime. Unlike the general tendency of two-dimensional materials that their band-gaps decrease with the increase in their thicknesses, the decoration of graphene to thin g-C₃N₄ nanosheets yielded the reduced band-gap. Fig. 3(c) and (d) shows magnified LDOS of Fig. 3(a) and (b), respectively, which agree well with each other. We attribute this seemingly counter-intuitive result to the strong coupling between g-C₃N₄ and graphene. As the thickness of g-C₃N₄ is sufficiently small for tunneling, we were able to observe weak signatures of a Dirac cone of the underlying graphene in both measured and calculated LDOSs. Even though this signature of graphene is significantly weaker than the resonance energy peaks of g-C₃N₄, it is sufficiently discernible to show that the energy locations of Dirac points vary depending on the atomic sites. This implies that charge imbalance exists at the graphene/g-C₃N₄ interface due to the strong coupling depending on the atomic registry which may induce the enhancement of dielectric function by calculations as reported previously [44]. We consider that the shift of Dirac cones is an evidence of the strong coupling between g-C₃N₄ and graphene, responsible for the reduction in the band-gap.

Further investigations were performed by KPFM measurements to elucidate the energy locations of the conduction and valence band edges, which are of crucial importance for HER and OER applications.

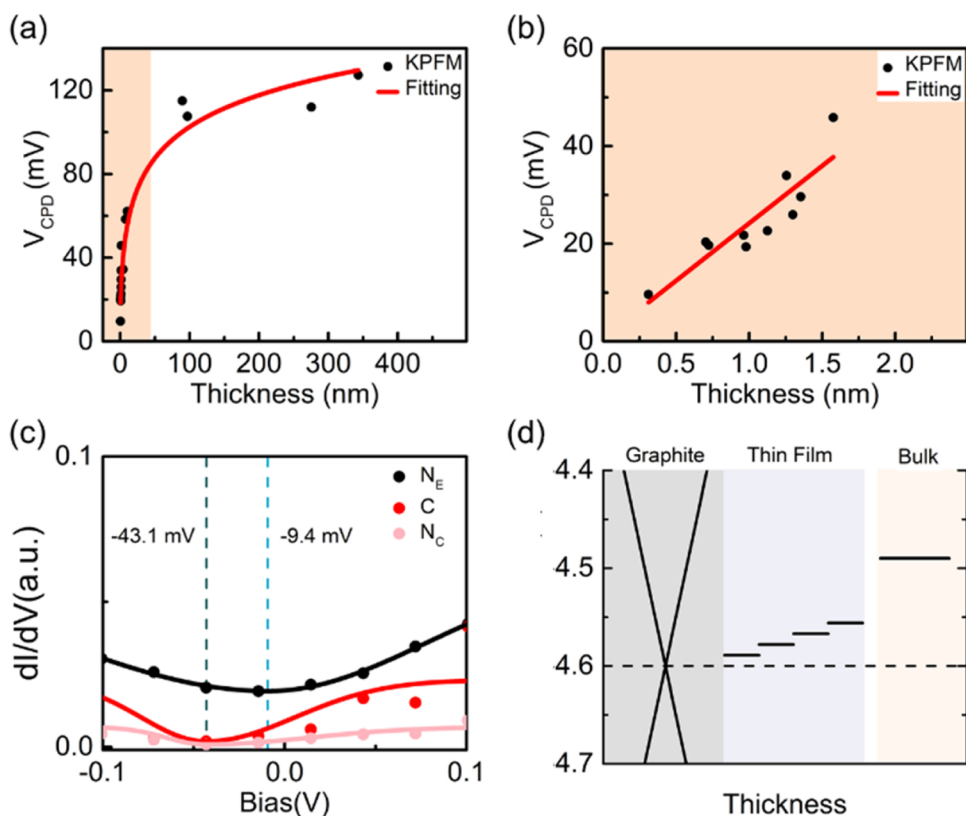


Fig. 4. Thickness-dependent work-function tuning of g-C₃N₄ nanosheets. (a) Statistical plot of CPD with different thicknesses of g-C₃N₄ nanosheets on HOPG, measured by KPFM. (b) Magnified plot from the colored region in (a) for thicknesses smaller than 2 nm; a linear dependence is observed. (c) Magnified plot of the measured LDOS for carbon and nitrogen atoms; the charge neutral points are indicated. (d) Schematic diagram of a Dirac point and charge neutral points for different g-C₃N₄ thicknesses.

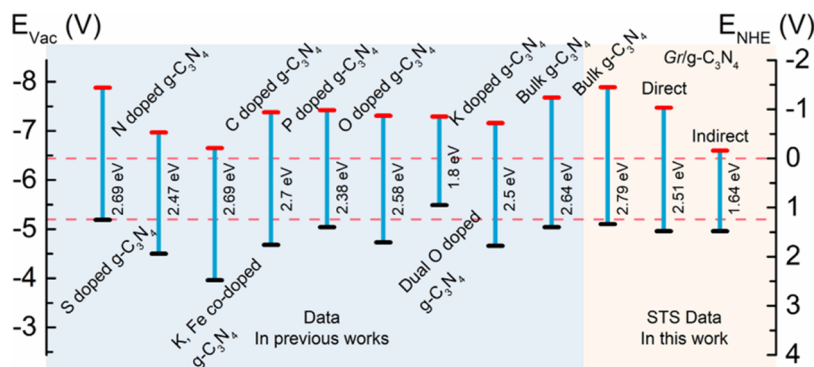


Fig. 5. Figure Caption Energy level diagram for various photocatalysts. The energy level diagrams of doped g-C₃N₄ [45–52] series were reported in previous studies. The measured values of various g-C₃N₄ structures are plotted for the bulk phase; the direct and indirect band-gaps of the graphene-decorated system are shown.

The spatial mapping of the thickness-dependent surface potential by KPFM, as well as atom-dependent LDOS measurements by STS, can reveal the energy alignments of g-C₃N₄/graphene heterostructures. Fig. 4(a) shows a statistical plot of contact potential difference (CPD) of KPFM measurements for different g-C₃N₄ thicknesses on HOPG, which is a good substrate for the estimation of potential difference considering its work-function of 4.6 eV. As shown in Fig. 4(b) which presents a magnified view of Fig. 4(a), while the bulk-phase g-C₃N₄ saturates to 120 mV, thin g-C₃N₄ nanosheets on HOPG exhibit a linear dependence of the CPD for thicknesses smaller than 2 nm with a value of 11 mV for monolayer g-C₃N₄. As partly explained in Fig. 3, the work-function change of the graphene-decorated g-C₃N₄ can be understood at the atomic scale. Fig. 4(c) further magnifies the spectra of Fig. 3(c) in the sample bias range of -100 mV to +100 mV. Although both N_E and N_C are located on top of hollow sites of the underlying graphene, they have different charge neutral points of -9.4 mV for N_E and -43.1 mV for N_C, which implies a strong atomic-registry-dependent interaction between g-C₃N₄ and graphene, as mentioned above.

This occurs as N_E is electron-rich, unlike N_C, owing to an extra pair of electrons that do not participate in atomic bonding. The shift of the charge neutral point by 9.4 mV from the Fermi level in Fig. 4(c) is very similar to the value of CPD in Fig. 4(b). As the surface potential is determined by electrons on the surface, the six N_E sites in the unit cell dominate the surface potential of the g-C₃N₄/graphene heterostructures. The energy locations of charge neutral points on C and N_C are shifted further away from the Fermi level owing to the in-plane electric field induced by the charge distribution of g-C₃N₄. We can see this energy shift not only Fig. 4(d) but also Figure S4(d)–(f). When compared with Figure S4(e) and (f), the energy structures of carbon of g-C₃N₄ and N_C are shifted by 200 mV, and N_E is shifted by 100 mV. These energy shifts are originated from the distortion of g-C₃N₄ while the nitrogen atoms at the edge (N_E) on hollow sites of graphene in our nitrogen-AB stacking configuration can maintain g-C₃N₄ in a planar phase in (d). Therefore, the work-function location could be understood by comparing the STS at the atomic scale and thickness-dependent KPFM data summarized in Fig. 4(d).

Fig. 5 presents an energy diagram showing the conduction and valence bands for well-known photocatalytic materials, including our measurements of g-C₃N₄/graphene with the corresponding band-gaps. The left ordinate represents the energy from the vacuum level, while the right ordinate represents the normal hydrogen electrode (N_{HE}) at pH = 0. The two horizontal dashed lines represent the energies for HER and OER. As summarized in this Figure, the metal-free photocatalyst of g-C₃N₄/graphene heterostructures can have band-gaps appropriate for visible-light applications and band alignments for HER and OER. The comparison with the other materials in this plot and other precious photocatalytic metals reveals that the g-C₃N₄/graphene heterostructure is a promising photocatalyst candidate for visible-light applications.

4. Conclusion

In the process which improvement of efficient precious metal free photocatalyst [35–41,45–54], the g-C₃N₄ epitaxially decorated with graphene was proposed as a photocatalyst for HER and OER applications. This heterostructure had a direct band-gap of 2.51 eV and indirect band-gap of 1.64 eV, representing the best fit to visible light. The band structures were obtained by STS measurements at the atomic scale, supported by DFT calculations. Band alignments appropriate for HER and OER could be confirmed by thickness-dependent CPD measurements by KPFM and atomic registry-dependent spectra by STS. Nitrogen atoms at the edge (N_E) were crucial to tune the surface potential associated with their extra pair of electrons with a direct band-gap. Moreover, N_E supported electronic transitions through an indirect band-gap to neighboring carbon atoms, while the other nitrogen and carbon atoms had indirect band-gaps. Therefore, the graphene-decorated g-C₃N₄ is a promising, efficient, metal-free, chemically stable, and mechanically robust photocatalyst for HER and OER in water-splitting under visible light.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.117850>.

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